

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
16 December 2004 (16.12.2004)

PCT

(10) International Publication Number
WO 2004/108639 A1

(51) International Patent Classification⁷: C07C 11/02,
5/48, B01J 23/56, 23/92, 37/02

(21) International Application Number:
PCT/GB2004/002140

(22) International Filing Date: 18 May 2004 (18.05.2004)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
0312968.1 5 June 2003 (05.06.2003) GB
0312970.7 5 June 2003 (05.06.2003) GB

(71) Applicant (for all designated States except US): BP
CHEMICALS LIMITED [GB/GB]; Chertsey Road,
Sunbury-on-Thames, Middlesex TW16 7BP (GB).

(72) Inventors: and

(75) Inventors/Applicants (for US only): LITTLE, Ian,
Raymond [GB/US]; 27W650 North Lane, Naperville,
IL 60540 (US). REID, Ian, Allan, Beattie [GB/GB];
12 Crowthorne Close, Southfields, London SW18 5RX
(GB). WILLIAMS, Vaughan, Clifford [GB/GB]; 88
Shaftesbury Crescent, Staines, Middlesex TW18 1QW
(GB).

(74) Agent: HYMERS, Ronald, Robson; BP International
Limited, Chertsey Road, Sunbury-on-Thames, Middlesex
TW16 7LN (GB).

(81) Designated States (unless otherwise indicated, for every
kind of national protection available): AE, AG, AL, AM,
AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN,
CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI,
GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE,

KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MI,
MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PH,
PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM,
TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM,
ZW.

(84) Designated States (unless otherwise indicated, for every
kind of regional protection available): ARIPO (BW, GI,
GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM,
ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, F,
FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, S,
SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ,
GW, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

— as to applicant's entitlement to apply for and be granted
a patent (Rule 4.17(ii)) for the following designations: AE,
AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ,
CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE,
EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS,
JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA,
MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM,
PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ,
TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM,
ZW. ARIPO patent (BW, GH, GM, KE, LS, MW, MZ, NA,
SD, SL, SZ, TZ, UG, ZM, ZW). Eurasian patent (AM, AZ,
BY, KG, KZ, MD, RU, TJ, TM). European patent (AT, BE,
BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE,
IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR). OAPI patent
(BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE,
SN, TD, TG)

— of inventorship (Rule 4.17(iv)) for US only

Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guide
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.

(54) Title: A CATALYST COMPRISING A METALIC SUPPORT AND A PROCESS FOR THE PRODUCTION OF OLEFINS

(57) Abstract: A catalyst capable of supporting combustion beyond the fuel rich limit of flammability comprising a catalytic component and a metallic support wherein the support is a metallic structured packing comprising a multiplicity of open-ended channels and which has been loaded with a non metallic coating, and a process for the production of an olefin, said process comprising passing a mixture of a hydrocarbon and an oxygen-containing gas over said catalyst to produce an olefin.

WO 2004/108639 A1

10/557697

IAP6 Rec'd PCT/PTO 22 NOV 2005

A CATALYST COMPRISING A METALLIC SUPPORT AND A PROCESS FOR
THE PRODUCTION OF OLEFINS

The present invention relates to a process for the production of olefins from hydrocarbons in which the hydrocarbons are treated to autothermal cracking.

Autothermal cracking is a route to olefins in which the hydrocarbon feed is mixed with oxygen and passed over an autothermal cracking catalyst. The autothermal
5 cracking catalyst is capable of supporting combustion beyond the fuel rich limit of flammability. Combustion is initiated on the catalyst surface and the heat required to raise the reactants to the process temperature and to carry out the endothermic cracking process is generated in situ. Generally the hydrocarbon feed and the oxygen is passed over a supported catalyst to produce the olefin product. Typically, the catalyst
10 comprises at least one platinum group metal, for example, platinum. The autothermal cracking process is described in EP 332289B; EP-529793B; EP-A-0709446 and WO 00/14035.

The catalyst supports are usually non metallic and are typically ceramic materials, usually in the form of foams, monoliths, pellets, beads, spheres, tablets and/or
15 extrudates. However whilst generally being chemically inert non metallic supports can often be unstable to thermal and physical shock which results in support cracking.

The catalyst support may also be metallic. Due to their malleable nature metallic supports do not exhibit support cracking but are often incapable of withstanding excessive front face temperatures that are produced in the autothermal reactor which
20 leads to oxidation and corrosion.

Consequently there is a need to provide an improved support that is both chemically inert and thermally stable.

It has now been found that the autothermal cracking process can be improved by employing a catalyst with a modified metallic support and which has a structure that provides a low pressure drop in the autothermal reactor.

Accordingly, the present invention provides a catalyst capable of supporting
5 combustion beyond the fuel rich limit of flammability comprising a catalytic component and a metallic support wherein the support is a metallic structured packing comprising a multiplicity of open-ended channels and which has been loaded with a non metallic coating.

The present invention also provides a process for the production of an olefin, said
10 process comprising passing a mixture of a hydrocarbon and an oxygen-containing gas over a catalyst as herein described above to produce said olefin.

Preferably, the catalyst component comprises a Group VIII B metal. Suitable Group VIII B metals include platinum, palladium, ruthenium, rhodium, osmium and iridium. Preferably, the Group VIII B metal is selected from rhodium, platinum,
15 palladium or mixtures thereof. Especially preferred are platinum, palladium or mixtures thereof. Typical Group VIII B metal loadings range from 0.01 to 50 wt%, preferably, from 0.01 to 20 wt%, and more preferably, from 0.01 to 10 wt%, for example 1-5 wt%, such as 3-5 wt%. Suitably, the first catalyst bed comprises platinum or palladium, especially platinum.

20 Preferably the catalyst component may be a promoted catalyst component such as a promoted Group VIII B metal catalyst. The promoter may be selected from the elements of Groups IIIA, IVA and VA of the Periodic Table and mixtures thereof. Alternatively, the promoter may be a transition metal; the transition metal being a different metal to the catalyst component, such as the Group VIII B metal(s) employed
25 as the catalytic component.

The promoter may also be selected from any of the lanthanide metal oxides.

Preferred Group IIIA metals include Al, Ga, In and Tl. Of these, Ga and In are preferred. Preferred Group IVA metals include Ge, Sn and Pb. Of these, Ge and Sn are preferred, especially Sn. The preferred Group VA metal is Sb. The atomic ratio of
30 Group VIII B metal to the Group IIIA, IVA or VA metal may be 1 : 0.1 - 50.0, preferably, 1 : 0.1 - 12.0, such as 1 : 0.3 - 5.

Suitable transition metal promoters may be selected from any one or more of

Groups IB to VIIIB of the Periodic Table. In particular, transition metals selected from Groups IB, IIB, VIB, VIIB and VIIIB of the Periodic Table are preferred. Examples of such transition metal promoters include V, Ni, Ta, Cr, Mo, W, Mn, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pt, Cu, Ag, Au, Zn, Cd and Hg. Preferred transition metal promoters are Mo, Rh, Ru, Ir, Pt, Cu and Zn, especially Cu. The atomic ratio of the Group VIIIB metal to the transition metal promoter may be 1: 0.1 - 50.0, preferably, 1:0.1 - 12.0.

Specific examples of promoted Group VIIIB metals for use as the promoted catalyst component include Pt/Ga, Pt/In, Pt/Sn, Pt/Ge, Pt/Cu, Pd/Sn, Pd/Ge, Pd/Cu and Rh/Sn. Where the Group VIIIB metal is Rh, Pt or Pd, the Rh, Pt or Pd may comprise between 0.01 and 5.0 wt %, preferably, between 0.01 and 3.0 wt %, and more preferably, between 0.5 and 3.0 wt % of the total weight of the catalyst. The atomic ratio of Rh, Pt or Pd to the Group IIIA, IVA, VA or transition metal promoter may be 1: 0.1 - 50.0, preferably, 1: 0.1 - 12.0. For example, atomic ratios of Rh, Pt or Pd to Sn may be 1: 0.1 to 50, preferably, 1: 0.1 - 12.0, more preferably, 1: 0.2 - 5.0 and most preferably, 1: 0.3 - 5.0. Atomic ratios of Pt or Pd to Ge may be 1: 0.1 to 50, preferably, 1: 0.1 - 12.0, and more preferably, 1: 0.5 - 8.0. Atomic ratios of Pt or Pd to Cu may be 1: 0.1 - 3.0, preferably, 1: 0.2 - 2.0, and more preferably, 1: 0.5 - 1.5.

For the avoidance of doubt, the catalyst component and the promoter may be present in any form, for example, as a metal, or in the form of a metal compound, such as an oxide.

The metallic support may be selected from any suitable metal. Suitable metals may include steel (mild and high carbon), stainless steel, Hastaloy, Ni-Chrome, Inconel, Monel, nickel, copper, iron, platinum, noble metals and their alloys, cobalt, FeCrAlY, NiCrAlY, or any alloy containing Y, Cr, Fe, Ni and Al e.g Kanthal, Incoloy MA956, or CoCrAlY. Small amounts of other elements, such as Si, Ti, Nb, Mo, W, Zr, Mg, Cu, may also be present.

Preferably the metal has a melting point of greater than 1200°C and most preferably the metal is selected from FeCrAlY, NiCrAlY, CoCrAlY, Ni-Chrome and (any grade of) Inconel and Monel.

The metallic support is a metallic structured packing which comprises a multiplicity of open-ended channels. This structure provides a low pressure drop compared to other types of support, such as extrudates and pellets, when used in an

autothermal reactor. This is advantageous since high pressure drop in the autothermal reactor can lead to excessive force being applied to the catalyst, which can lead to structural collapse.

5 The metallic support may be in the form of a foam but is preferably in the form of a channeled monolith.

The structural dimensions of the support type may also vary.

Wherein the support is in the form of a foam, the foams usually have a pore size in the range of 10 pores per inch (ppi) to 100ppi and preferably between 30 to 45ppi. These foams typically have a density of from between 60% to 99% of theoretical
10 density of a fully dense material.

Wherein the support material is in the form of a monolith the monolith is usually provided with regular channels. These channels may be of any suitable shape the preferred ones being square, rectangular, triangular, hexagonal and circular. Preferably the monolith is a honeycomb monolith. Typically the channels do not pass directly
15 through the monolith and usually the channels provide a complex passageway through the monolith. Usually the monolith has between 2000cpi (cells per inch) to 5cpi and preferably between 1000cpi to 10cpi.

The support preferably comprises a series of blocks or layers that tessellate together to leave no gaps. Preferably these blocks or layers are tiled within the reactor in
20 different directions and most preferably in a manner such that tiles of a layer either above or below do not exactly overlap with any neighbouring layer.

The non metallic coating is usually a ceramic material which may be any oxide or combination of oxides that is stable at high temperatures of, for example, between 600°C and 1200°C. The ceramic material preferably has a low thermal expansion co-
25 efficient, and is resistant to phase separation at high temperatures.

Suitable ceramic materials include alumina, silica-alumina, a combination of alumina and mullite, lithium aluminium silicate, cordierite, silicon carbide, zirconia toughened alumina, partially stabilized zirconia, fully stabilized zirconia, spinel, chromia, titania, aluminium titanate, or any combination of the above.

30 The non metallic coating may be loaded onto the metallic support by any method known in the art. In particular the non-metallic coating may be loaded onto the support by any one of the following methods; aluminizing, chemical vapour deposition, sputter

coating and washcoating.

Wherein the non metallic coating is alumina, aluminizing deposits aluminium metal onto the surface layer of the metallic support. Usually aluminizing comprises heating the metallic support in a crucible with aluminium powder. The aluminium deposited upon the surface of the metallic support is then oxidized to form alumina.

Wherein chemical vapour deposition is used to provide a non-metallic coating on the metallic support this usually involves the thermal decomposition of a volatile material onto the surface of a heated metallic support.

Wherein sputter coating is used to provide a non-metallic coating on the metallic support the metallic support is spray coated with a fine particulate material which typically contains some sort of binder such that it sticks to the surface of the support. Sputter coating may be performed by arc or laser ablation.

In a preferred embodiment of the invention washcoating is used to provide a non-metallic coating on the metallic support. Washcoating involves providing a slurry of the non metallic coating which is then poured through/over the metallic support. Typically the slurry of the non metallic coating is a ceramic coating and is preferably an alumina colloidal suspension with a carefully defined viscosity and particle size.

Wherein aluminizing is used the thickness of the non metallic coating is usually between 10-200 μ m and preferably between 50-100 μ m.

Wherein sputter coating is employed the thickness of the non metallic coating is usually between 10 μ m-2mm and preferably between 0.1-1mm.

Usually the % weight of coating relative to the weight of support is less than 5wt%, and preferably less than 3wt%.

Preferably substantially all of the metallic support is coated with the non metallic coating.

The catalyst component employed in the present invention may be loaded onto the coated metal support by any method known in the art. For example, gel methods and wet-impregnation techniques may be employed. Typically, the support is impregnated with one or more solutions comprising the metals, dried and then calcined in air. The support may be impregnated in one or more steps. Preferably, multiple impregnation steps are employed. The support is preferably dried and calcined between each impregnation, and then subjected to a final calcination, preferably, in air. The calcined

support may then be reduced, for example, by heat treatment in a hydrogen atmosphere.

Preferably when the catalyst is positioned within the autothermal cracking reactor a non catalytic resistance zone is located upstream of the catalyst. The resistance zone usually comprises a network of capillaries or channels and most preferably the resistance zone comprises a porous material and advantageously the porous material is a non metal e.g. a ceramic material. Suitable ceramic materials include lithium aluminium silicate (LAS), alumina (α - Al_2O_3), yttria-stabilised zirconia, alumina titanate. A preferred porous material is alpha alumina. The porous material may be in the form of spheres, other granular shapes or ceramic foams. Typically the resistance zone has between 10-60 pores per square inch, preferably between 20-50 pores per square inch and most preferably between 30-45 pores per square inch.

The process of the present invention may be used to convert both liquid and gaseous hydrocarbons into olefins. Suitable liquid hydrocarbons include naphtha, gas oils, vacuum gas oils and mixtures thereof. Preferably, however, gaseous hydrocarbons such as ethane, propane, butane and mixtures thereof are employed. Suitably, the hydrocarbon is a paraffin-containing feed comprising hydrocarbons having at least two carbon atoms.

The hydrocarbon feed is mixed with any suitable oxygen-containing gas. Suitably, the oxygen-containing gas is molecular oxygen, air, and/or mixtures thereof. The oxygen-containing gas may be mixed with an inert gas such as nitrogen or argon.

Additional feed components may be included, if so desired. Suitably, hydrogen, carbon monoxide, carbon dioxide or steam may be co-fed into the reactant stream.

Any molar ratio of hydrocarbon to oxygen-containing gas is suitable provided the desired olefin is produced in the process of the present invention. The preferred stoichiometric ratio of hydrocarbon to oxygen-containing gas is 5 to 16, preferably, 5 to 13.5 times, preferably, 6 to 10 times the stoichiometric ratio of hydrocarbon to oxygen-containing gas required for complete combustion of the hydrocarbon to carbon dioxide and water.

The hydrocarbon is passed over the catalyst at a gas hourly space velocity of greater than $10,000 \text{ h}^{-1}$, preferably above $20,000 \text{ h}^{-1}$ and most preferably, greater than $100,000 \text{ h}^{-1}$. It will be understood, however, that the optimum gas hourly space velocity will depend upon the pressure and nature of the feed composition.

Preferably, hydrogen is co-fed with the hydrocarbon and oxygen-containing gas into the reaction zone. The molar ratio of hydrogen to oxygen-containing gas can vary over any operable range provided that the desired olefin product is produced. Suitably, the molar ratio of hydrogen to oxygen-containing gas is in the range 0.2 to 4, preferably, in the range 1 to 3.

Hydrogen co-feeds are advantageous because, in the presence of the catalyst, the hydrogen combusts preferentially relative to the hydrocarbon, thereby increasing the olefin selectivity of the overall process.

Preferably, the reactant mixture of hydrocarbon and oxygen-containing gas (and optionally hydrogen co-feed) is preheated prior to contact with the catalyst. Generally, the reactant mixture is preheated to temperatures below the autoignition temperature of the reactant mixture.

Advantageously, a heat exchanger may be employed to preheat the reactant mixture prior to contact with the catalyst. The use of a heat exchanger may allow the reactant mixture to be heated to high preheat temperatures such as temperatures at or above the autoignition temperature of the reactant mixture. The use of high pre-heat temperatures is beneficial in that less oxygen reactant is required which leads to economic savings. Additionally, the use of high preheat temperatures can result in improved selectivity to olefin product. It has also been found that the use of high preheat temperatures enhances the stability of the reaction within the catalyst thereby leading to higher sustainable superficial feed velocities, and also reduces the thermal gradient experienced across the catalyst.

The process of the present invention may suitably be carried out at a catalyst exit temperature in the range 600°C to 1200°C, preferably, in the range 850°C to 1050°C and, most preferably, in the range 900°C to 1000°C.

The process of the present invention is usually operated at a pressure of greater than 0.5barg. Preferably the autothermal cracking process is operated at a pressure of between 0.5-40barg and advantageously between 10-30barg e.g. 15-25barg.

The reaction products are preferably quenched as they emerge from the reaction chamber to avoid further reactions taking place. Usually the product stream is cooled to between 750-600°C within less than 100milliseconds of formation, preferably within 50milliseconds of formation and most preferably within 20milliseconds of formation

e.g. within 10 milliseconds of formation.

Wherein the autothermal cracking process is operated at a pressure of 5-20 barg usually the products are quenched and the temperature cooled to between 750-600°C within 20 milliseconds of formation. Advantageously wherein the autothermal cracking process is operated at a pressure of greater than 20 barg the products are quenched and the temperature cooled to between 750-600°C within 10 milliseconds of formation.

The invention will now be illustrated by the following examples.

Examples

Preparation of Catalysts

10 Comparative Catalyst 1

FeCrAlY foam blocks, comprising (by weight) approximately 73% iron, 20% chromium, 5% aluminium and 2% yttrium (III) oxide, in the shape of cylinders having dimensions of 15mm diameter by 25mm depth, and pore size of 30 pores per inch (ppi) were purchased from Porvair Advanced Materials.

15 The foams were repeatedly impregnated by immersion in a solution of tetraamineplatinum (II) chloride and copper (II) nitrate hexahydrate, said solution containing sufficient of each respective salt to achieve a nominal Pt loading of 3wt% and a nominal Cu loading of 1wt% if all the metal in the respective salts were incorporated into the final catalyst formulation.

20 Between impregnations excess solution was removed from the foams, which were then dried in air at ca. 120°C for approximately 20 minutes. After all the metal salts had been incorporated the foams were calcined in air at 600°C for approximately 6 hours, cooled to room temperature, and then reduced under a flow of 50vol% hydrogen/50vol% nitrogen at 750°C and at a flow rate of 2nl/min for 1 hour.

25 Catalyst A

As for Catalyst 1, FeCrAlY foam blocks comprising (by weight) approximately 73% iron, 20% chromium, 5% aluminium and 2% yttrium (III) oxide, in the shape of cylinders having dimensions of 15mm diameter by 25mm depth, and having a pore size of 30 pores per inch (ppi) were purchased from Porvair Advanced Materials.

30 The foams were washcoated with a gamma alumina washcoat and calcined before being loaded with Pt and Cu at a nominal Pt loading of 3wt% and a nominal Cu loading of 1wt% (assuming all the metal were incorporated into the final catalyst formulation).

The foams were subsequently calcined in air at 600°C for approximately 6 hours, cooled to room temperature, and then reduced under a flow of 50vol% hydrogen/50vol% nitrogen at 750°C and at a flow rate of 2nl/min for one hour.

Catalyst Testing

5 Catalyst testing was performed at atmospheric pressure (0 barg) in an autothermal reactor comprising a steel reactor in an electrically heated furnace.

The catalyst blocks were positioned in the reactor between two LAS heat shields. Two blocks of catalyst were loaded in sequential fashion into the reactor for each test, to give a total catalyst bed of 50mm depth, and the reactor heated to 850°C. Ethane
10 (6.09nl/min), hydrogen (5.48nl/min), nitrogen (1.61nl/min) and oxygen (2.74nl.min) were supplied from cylinders via mass flow controllers into two manifolds, one for oxygen, the second for the other gases. The two gas streams were pre-heated to around 100°C and then mixed immediately before the catalyst. The product gases were sampled and analysed by gas chromatography. The results are shown in Table 1 and Table 2.

15

20

25

30

Table 1: Ethylene yield (g/100g hydrocarbon) with time on stream for Comparative Catalyst 1 and Catalyst A.

Time on stream hours	Ethylene yield (g/100g)	
	Comparative Catalyst 1	Catalyst A
1.75	-	56.6
2.5	51.5	-
4.75	51.35	-
5.0	-	56.7
9.25	52.3	-
21.75	-	56.4
25.2	54.5	-
26.0	-	56.3
32.0	54.3	-
44.5	-	56.6
48.0	-	56.7
48.5	55.0	-
51.7	-	56.7
52.7	55.44	-
58.3	53.4	-
68.5	-	56.6
72.2	55.2	-
74.4	-	56.1

Table 2: Product distribution at 48 hours on stream for Comparative Catalyst 1 and Catalyst A.

	Comparative Catalyst 1	Catalyst A
Ethane Conversion (%)	78.8	81.0
Yield (g/100g hydrocarbon):		
Hydrogen	7.60	7.10
Water	40.2	43.2
Methane	5.27	6.71
CO	14.2	14.8
CO ₂	5.68	1.58
Ethylene	55.0	56.7
Ethane	21.2	19.0
Acetylene	0.58	0.94

Table 1 shows that, relative to a non-washcoated metallic foam, Catalyst A results in an increased ethylene yield. Table 2 shows that, relative to a non-washcoated metallic foam, and in addition to an increased ethylene yield, Catalyst A also results in a significantly reduced carbon dioxide yield.

Claims:

1. A catalyst capable of supporting combustion beyond the fuel rich limit of flammability comprising a catalytic component and a metallic support wherein the support is a metallic structured packing comprising a multiplicity of open-ended channels and which has been loaded with a non metallic coating.
- 5 2. A catalyst as claimed in claim 1, wherein the catalyst component comprises a Group VIIIB metal.
3. A catalyst as claimed in claim 1 or claim 2, wherein the metallic support is selected from FeCrAlY, NiCrAlY, CoCrAlY, Ni-Chrome, Inconel and Monel.
4. A catalyst as claimed in any one of the preceding claims, wherein the metallic
10 support is in the form of a foam having a pore size in the range of 10 pores per inch (ppi) to 100ppi.
5. A catalyst as claimed in any one of claims 1 to 4, wherein the metallic support is in the form of a monolith having between 2000cpi (cells per inch) to 5cpi.
6. A catalyst as claimed in any one of the preceding claims, wherein the metallic
15 support comprises a series of blocks or layers that tessellate together to leave no gaps.
7. A catalyst as claimed in any one of the preceding claims, wherein the non metallic coating is a ceramic material selected from alumina, silica-alumina, a combination of alumina and mullite, lithium aluminium silicate, cordierite, silicon carbide, zirconia toughened alumina, partially stabilized zirconia, fully stabilized zirconia, spinel,
20 chromia, titania, aluminium titanate, or any combination of the above.
8. A catalyst as claimed in any one of the preceding claims, wherein the non-metallic has been loaded onto the support by any one of the following methods; aluminizing,

chemical vapour deposition, sputter coating and washcoating.

9. A catalyst as claimed in claim 8, wherein washcoating is used to provide the non-metallic coating on the metallic support.

10. A process for the production of an olefin, said process comprising passing a

5 mixture of a hydrocarbon and an oxygen-containing gas over a catalyst as claimed in any one of claims 1 to 9.

11. A process as claimed in claim 10, wherein hydrogen is co-fed with the hydrocarbon and oxygen-containing gas to the reaction zone.

12. A process as claimed in claim 10 or claim 11, wherein a non catalytic resistance
10 zone is located upstream of the catalyst.

13. A process as claimed in any one of claims 10 to 12, wherein the ratio of hydrocarbon to oxygen-containing gas is 5 to 16, times the stoichiometric ratio of hydrocarbon to oxygen-containing gas required for complete combustion of the hydrocarbon to carbon dioxide and water.

14. A process as claimed in any one of claims 10 to 13, wherein the process is
15 operated at a pressure of between 10-30barg.

20

25

30

INTERNATIONAL SEARCH REPORT

International Application No.

GB2004/002140

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C07C11/02 C07C5/48 B01J23/56 B01J23/92 B01J37/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07C B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 713 725 A (TOYOTA MOTOR CO LTD ; CATALER IND CO (JP)) 29 May 1996 (1996-05-29) page 5, line 17 - page 7, line 59; claims; examples	1-9
X	EP 0 332 289 A (BRITISH PETROLEUM CO PLC) 13 September 1989 (1989-09-13) page 2, line 47 - page 3, line 11; claims; examples; tables	1-14
X	US 6 395 944 B1 (GRIFFITHS DAVID CHARLES ET AL) 28 May 2002 (2002-05-28) column 2, line 64 - column 3, line 16; claims; examples; tables	1-14
	----- -/-	

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- *G* document member of the same patent family

Date of the actual completion of the international search

27 July 2004

Date of mailing of the international search report

09/08/2004

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel: (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

de Cauwer, R

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/GB2004/002140

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 1 109 876 A (DOW CHEMICAL CO) 27 June 2001 (2001-06-27) page 3, line 16 - page 6, line 55; claims; examples -----	1-14
X	YOKOYAMA C ET AL: "PLATINUM-TIN AND PLATINUM-COPPER CATALYSTS FOR AUTOTHERMAL OXIDATIVE DEHYDROGENATION OF ETHANE TO ETHYLENE" CATALYSIS LETTERS, BALTZER, SCIENTIFIC PUBL, BASEL, CH, vol. 38, no. 3/4, 1 May 1996 (1996-05-01), pages 181-188, XP000590672 ISSN: 1011-372X the whole document -----	1-14

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB2004/002140

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0713725	A	29-05-1996	JP 8206516 A	13-08-1996
			DE 69520777 D1	31-05-2001
			DE 69520777 T2	11-10-2001
			EP 0713725 A2	29-05-1996
			US 5898016 A	27-04-1999
EP 0332289	A	13-09-1989	AU 2970489 A	14-09-1989
			CA 1316946 C	27-04-1993
			CN 1038271 A ,B,	27-12-1989
			DE 68921907 D1	04-05-1995
			DE 68921907 T2	28-09-1995
			EP 0332289 A2	13-09-1989
			JP 1272534 A	31-10-1989
			JP 2516676 B2	24-07-1996
			NO 890862 A ,B,	11-09-1989
			NZ 227922 A	29-01-1990
			US 4940826 A	10-07-1990
			US 5105052 A	14-04-1992
			ZA 8901729 A	28-11-1990
US 6395944	B1	28-05-2002	AU 751027 B2	08-08-2002
			AU 5642199 A	03-04-2000
			BR 9913555 A	05-06-2001
			EP 1129056 A1	05-09-2001
			WO 0015587 A1	23-03-2000
			US 2002143220 A1	03-10-2002
EP 1109876	A	27-06-2001	AT 244695 T	15-07-2003
			AU 757855 B2	06-03-2003
			AU 5800099 A	27-03-2000
			BR 9913437 A	22-05-2001
			CA 2339762 A1	16-03-2000
			DE 69909490 D1	14-08-2003
			DE 69909490 T2	27-05-2004
			EP 1109876 A1	27-06-2001
			JP 2002524606 T	06-08-2002
			CN 1315931 T	03-10-2001
			ES 2203178 T3	01-04-2004
			ID 27736 A	26-04-2001
			US 2002087042 A1	04-07-2002
			WO 0014180 A1	16-03-2000
			US 6365543 B1	02-04-2002